Our ref.: EP 13 283 - hs

TRANSLATION INTO ENGLISH OF:

D1A, Sections 3.1 and 3.2, Figs. 2, 3

3.1 The thermal regime in the gradient freezing method

In the oriented crystallization according to the Bridgman method, three principles can be employed for initiating the solidification process:

- movement of the furnace with stationary charge,
- movement of the sample with stationary furnace,
- electronically controlled travel of the temperature field (gradient-freezing method).

Using multi-zone furnaces, the last-mentioned method is particularly suited for setting the necessary thermal conditions, which differ considerably in time and place, during growth [4].

The crystallization tests proper were concentrated on the growth of GaAs monocrystals according to the gradient freezing method. The experimental regime consists in the following:

- furnace with separately heated zones,
- molten quartz ampoule with the crucible for the GaAs charge,
- temperature profile with 3 plateaus:
 - plateau of the arsenic source T_α (620°C),
 - lower growth plateau T_υ (1200°C)
 - upper growth plateau To (1260°C) [5, 6].

The position of the crystallization front T_M (1240°C) is between T_O and T_U . Crystallization was carried out by programmed decrease in the heating power

(power-down method) or by the programmed lowering of the set temperatures of the zones in the gradient range between T_0 and T_U . In both cases graded heating power profiles that are variable in time and may lead to temperature distributions with varying local temperature gradients in the sample are created at the predetermined set temperatures. According to relation (1) this would also lead to variable crystallization rates with negative consequences for the stability of the growth process despite a constant temperature decrease G_t .

These phenomena, however, can be avoided through tests regarding the choice of the conditions as to apparatus and experiments. Model calculations are suited and helpful for minimizing the time-consuming and expensive experimental efforts. A computing program which permits the determination of the basic temperature curve with given set temperatures for the position of the thermocouple was used for this purpose.

A typical result is shown in Fig. 2, which in terms of quality corresponds to the results of experimental investigations. The following information can be derived:

- The set temperatures (T_{set}) are not reached in zones 4 and 9 because the necessary heating powers (P) are above the admissible heating powers (P_{admissible}).
- In zone 3 the heating power (P_{actual}) is near 0, so that the thermal regime does also not correspond to the set temperatures, but is only defined by the irradiation from the hotter region.
- The temperature gradients in the regions adjoining the plateaus are much flatter than the predetermined values.
- In the plateau region the set temperatures are almost reached.
- At the edge of the plateau the set values exceed or fall short of the temperatures. This may lead to increased thermal loads in the heating conductors and to deformations in the temperature profile of the charge.

These phenomena must be heeded so as to be able to correctly set the thermal conditions that cannot be accessed in the interior of the charge by direct measurements.

Conditions during growth of GaAs 3.2

Fig. 3 shows a scheme of the apparatus used for growing GaAs crystals with the vertical gradient-freezing method. Fig. 4 shows a grown GaAs crystal. The experimental thermal conditions were plotted in Fig. 5 into the v-G_t-G_x diagram derived from relation (2).

It has been confirmed that the region given by the coordinates:

 $G_x = 1 \text{ K/cm}$

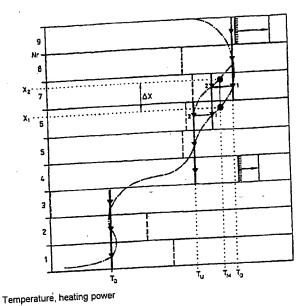
- 10 K/cm

 $G_t = 6 \cdot 10^{-5} \text{ K/s}$

- 3 10⁻³ K/s

 $v = 6 \cdot 10^{-5} \text{ cm/s}$ $-3 \cdot 10^{-4} \text{ cm/s}$ defines the conditions suited for growing GaAs with the gradient freezing method [7]. Curve 1 characterizes the maximum crystallization rate calculated from relation (2). To exploit the possible efficiency of the process to the maximum degree, the thermal conditions are often chosen such that the crystallization rate is within the range of said maximum value. The boundary condition for constitutional supercooling was calculated for the dopant Si. While the dopant concentrations of 10¹⁸ cm⁻³ (curve 3) and 10¹⁷ cm⁻³ (curve 4) do not endanger the crystallization process yet, constitutionally caused inhomogeneities and disturbances of the monocrystalline growth must be expected at concentrations of 10¹⁹ cm⁻³ (curve 2).

The growing conditions for GF-CdTe are also within the defined range. The Czochralski method can be carried out with a better blending of the melt and at much higher temperature gradients, thus permitting higher crystallization rates as well, which is however accompanied by a deteriorated real structure.



Heating zone

Fig. 2. Thermal conditions in the gradient freezing process (temperatures T:
--- T(actual) -▶- T(set) -position of the phase boundary (x), ▶ position of the thermocouples 1, 2 of successive technological steps, heating powers P:
---P(actual), ⊥⊥⊥⊥
P(admissible), ____ P (set)

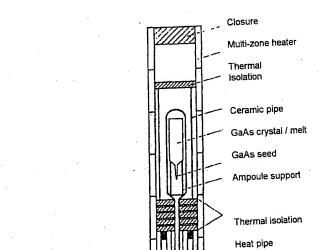


Fig. 3. Vertical gradient-freezing apparatus (schematic)

As source

Closure